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Surface Modification Energized by FIB: The Influence of Etch Rates & Aspect Ratio on Ripple Wavelengths

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ABSTRACT

Ion beams have been used to modify surface topography, producing nanometer-scale modulations (and even subnanometer ripples in this work) that have potential uses ranging from designing self-assembly structures, to controlling stiction of micromachined surfaces, to providing imprint templates for patterned media. Modern computer-controlled Focused Ion Beam tools enable alternating submicron patterned zones of such ion-eroded surfaces, as well as dramatically increasing the rate of ion beam processing. The DualBeam FIB/SEM also expedites process development while minimizing the use of materials that may be precious (Diamond) and/or produce hazardous byproducts (Beryllium). A FIB engineer can prototype a 3-by-3-by-3 matrix of variables in tens of minutes and consume as little as zeptoliters of material; whereas traditional ion beam processing would require tens of days and tens of precious wafers. Saturation wavelengths have been reported for ripples on materials such as single crystal silicon or diamond (~200nm); however this work achieves wavelengths >400nm on natural diamond. Conversely, Be can provide a stable and ordered 2-dimensional array of <40nm periodicity; and ripples <0.4nm are also fabricated on carbon surfaces and quantified by HR-TEM and electron diffraction. Rippling is a function of material, ion beam, and angle; but is also controlled by chemical environment, redeposition, and aspect ratio. Ideally a material exhibits a constant yield (atoms sputtered off per incident ion); however, pragmatic FIB processes, coupled with the direct metrological feedback in a DualBeam tool, reveal etch rates do not remain constant for nanometer-scale processing. Control of rippling requires controlled metrology, and robust software tools are developed to enhance metrology. *In situ* monitoring of the influence of aspect ratio and redeposition at the micron scale correlates to the rippling fundamentals that occur at the nanometer scale and are controlled by the boundary conditions of FIB processing.

INTRODUCTION

The Focused Ion Beam tool has migrated from circuit-edit functions in the semiconductor fab, to site-specific sample preparation for TEM, to micromachining and prototyping, to research. As a DualBeam FIB/SEM with *in situ* metrology, FIB enables research to progress faster while synergistically opening new doors for FIB use. Furthermore, FIB allows development and study directly at the nanometer level, as opposed to many new processes that start big and then have problems scaling down. Direct prototyping at the nanometer also consumes little material on a substrate, which is often an expensive, limited and irreproducible entity for research.

Ripples grow. When an energetic ion beam impinges an atomically flat surface, morphological instabilities arise leading to self-organizing topography. This means ripples grow where they were not [1,2]. Numerous processing variables affect ripples; e.g. atomic species of incident ion and surface, energy, angle, dose, temperature, crystallography, as well as FIB parameters that control scanning and boundary conditions arising from site specificity [3-6]. Historically, roughness induced by ion etching was bad; and its mitigation (scanning, rotation, etc.) was attempted to improve Auger depth profiling [7] and to improve TEM sample preparation [8]. However, more recent control, metrology, and

understanding of the ion/surface interactions [4-6, 9-11] predict these modulations will have utility for nanostructural processing. A general engineering concern remains, when do ripples quit growing? Can ripples be made larger, and can they be restrained and made smaller?

FIB has a primary function of etching or machining surfaces, and the designed 30 keV Ga ions attempt to maximize yields (atoms off per incident ion) by simultaneously interacting with several topmost layers. However, this leads to a disrupted zone (sometimes amorphous) in which significant atom motion occurs below, at, and above the surface [6]. FIB processing is very reproducible, and ideally the FIB etches at a constant rate (for a given material). However, yield can change due to many reasons; some deliberate such as angle of incidence and chemical enhancement [11,12], some unintentional such as aspect ratio and redeposition [13]. Even the growing ripples themselves lead to a change in yield [1,9]; and conversely, factors which change yield can lead to changes in ripple wavelength [13].

EXPERIMENTAL PROCEDURES & RESULTS

Surface modulations are created by ion sputter etching with a FIB (model FEI-NOVA600-DualBeam) with 30keV Ga⁺ ions. The concentric/eucentric stage of this tool enables versatile tilting experiments, allowing for ion beam etching at all possible incident angles [5, 11, 13] and also allowing for SEM metrology at multiple orientations [13]. For the diamond experiments, a single crystal, gem-quality diamond is used, which has numerous facets to study the effects of crystal orientation. A second sample is a CVD-coating on a SiC fiber. The coating is cross-sectioned, as per TEM sample preparation, by normal and 30° orientations of FIB processing. A third material is a polycrystalline rolled sheet of metal that had been mechanically polished prior to FIB sputter erosion. The NOVA600-FIB has versatile computer control of FIB scanning parameters. In addition, a gas injection system (GIS) provides chemical-enhanced ion etching using water. The needle of the GIS has an opening within 150 microns of the surface of the sample and enables a pressure at the surface that is $\sim 10^3$ higher than the base pressure of the system. The monitored base pressure of the vacuum system ranges from 10^{-5} to 10^{-4} Torr during chemical-enhanced etching. (I.e. vapor pressure at the sample surface is as high as 10^{-1} Torr.) Water vapor reacts with the topmost layer of diamond and expedites the ion milling process. Diamond is the optimal tool-bit; and micromachining operations often request small diamond bits. FIBs can nanomachine diamonds, however the low yield (~ 2) has led to several attempts to enhance yield [11-13].

Figure 1 presents three SEM images acquired of diamond surfaces having been FIB-etched at inclined angles. Adams and co-workers [e.g. 11] have plotted the effects of angle and chemistry on ripple amplitude (as well as corresponding enhancement in yield). Ion etching normal and near normal produces smooth surfaces (even smoother than the initial diamond [11, 13]). Upwards of 30° (away from normal incidence), the eroded surfaces exhibit "ripples" perpendicular to the angle of inclination [2, 11] (e.g. Fig. 1a), with a reported saturation wavelength of $\sim 220\text{nm}$ at 60° [10]. At $\sim 70^\circ$, the ripples switch to "steps" [11]. Often chemical-assisted FIB is used to provide smoother surfaces, and reduced roughness has been reported for water-enhanced FIB etching of diamond [11, 12]. In this work, the wet FIBing can also produce surface modulations; however rather than fluence or chemistry, the wavelengths of ripples appear to correlate with aspect ratio. Figures 1d and 1e plot for a single angle, 60°. (The addition of chemistry to the FIB can lead to many complexities and instabilities [13] all of which could make the FIBing less reproducible, and FIB instabilities can sometimes lead to ripple destruction.) Similarly, the transition from ripple-to-step depends not only on angle ($\sim 70^\circ$ or 60° in Fig. 1a, 1b) but also on aspect ratio.

Yield can be enhanced by increasing the angle of incidence or by chemical enhancement [11, 12]. However, yield diminishes with aspect ratio for various angles of incidence and with water vapor (Fig.2). Unfortunately the two parameters used to increase yield also make it more susceptible to dropping with aspect ratio. It is not surprising that a hole FIBed at a 45-degree angle cannot go much deeper than its width before the rate of deepening is diminished. Material has a difficult time getting out of a hole and redeposition causes the effective etch rate to slow down. Thus the plot of dropping etch rates in Fig. 2 may be turned upside-down and defined as the increase in redeposition with aspect ratio.

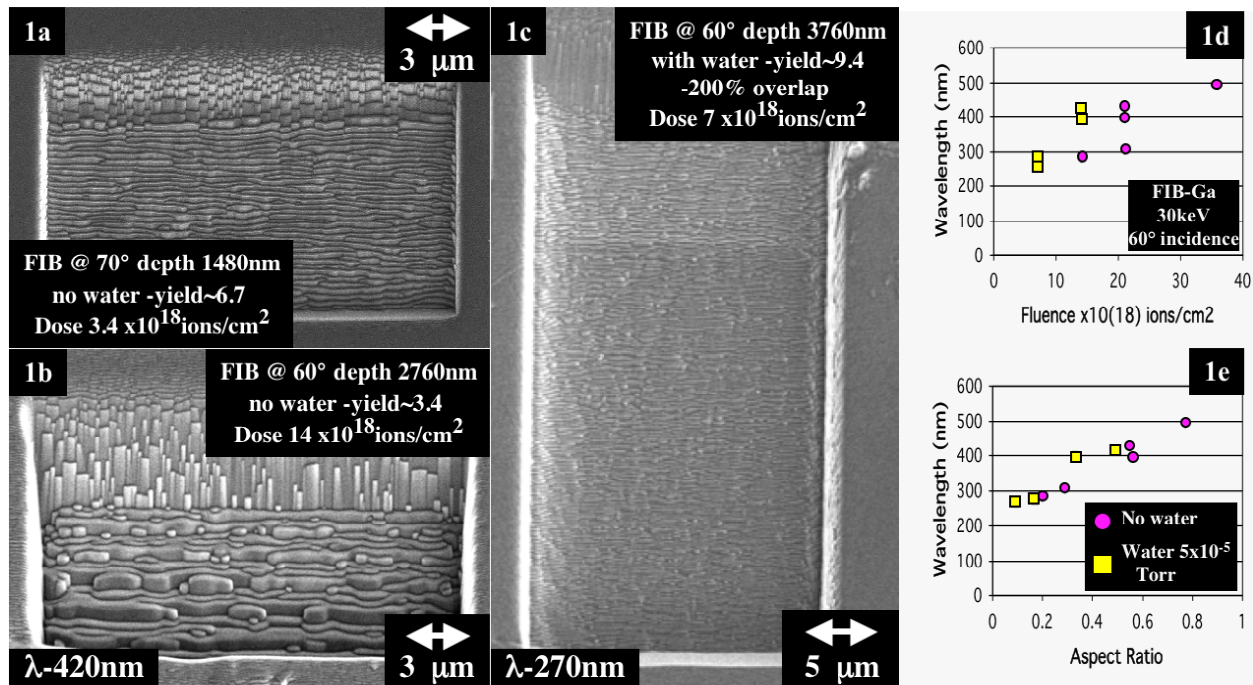


Figure 1: SEM images of natural diamond after FIBing at different inclinations and water vapor pressures. Ion etched surfaces exhibit smooth, rippled (a), or step (b) topography, typically with increasing angle [11]. Chemical enhanced ion etching need not mitigate ripples (c); and wavelengths need not saturate with fluence (d); but rather modulation and wavelength can correlate to aspect ratio (e) and redeposition, especially for FIB of inclined surfaces.

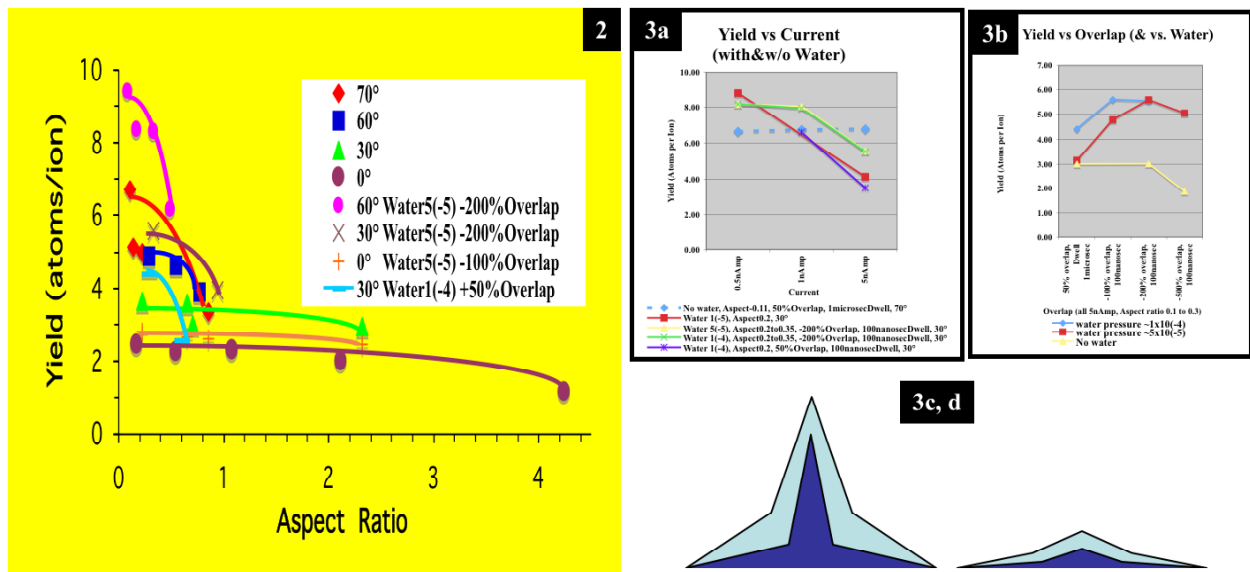


Figure 2: Ion etch rates are enhanced by increasing angle of incidence (0° = normal), and also by chemical additions (water vapor for the case of diamond); however, yield decreases with aspect ratio and more so for the enhanced cases [13]. Figure 3: Yield is typically constant for a wide range of FIB processing parameters, however, adding chemistry creates a complex interdependence. (a) Yield is chemically enhanced only for lower ion currents. (Note dotted blue of "no water" condition is at 70° incidence; 0° incidence has a yield of ~2.) (b) Overlap (negative) has the most impact on chemically enhanced yields. (c,d) Intensity profiles of the FIB beams include significant tails that become more extensive for smaller spots. The tails, regions of lower current, experience a greater % chemical enhancement, and become more influential for negative overlap FIB (digital) scanning.

The numerous FIB computer controls enable a wide range of processing variables, such as current from 1pA to 20000pA, dwell time, spot size, overlap, scan pattern, etc. Ion sputter yield is typically constant over a wide window of these parameters. (E.g. double the current and the FIB machines twice as fast, but the yield remains constant.) However, the inclusion of water vapor creates a strong interdependence of other FIB processing variables. Figures 3a and 3b plot yield enhancement due to water as functions of two FIB parameters, current and overlap, respectively. (Plots of other parameters [13] all indicate too much water becomes a detriment to etching.) Water enhancement works because the water vapor reacts with the top surface layer of diamond atoms and alters the strong sp³ bond. It is easier for the FIB Ga ion to etch away this material. However, the subsequent FIB ion now sees the next layer of atoms that still have strong bonds and etching slows down. An ideal FIB would etch each pixel only long enough to remove the affected layer and then move to the next pixel. Modern FIBs have a minimum dwell time of ~100 nanoseconds, however, that is >1000 times too long. Reducing current also accentuates chemical yield enhancement; however, the total etch rate suffers [13]. A negative overlap dramatically enhances yield in the presence of water vapor because the skipped pixels are exposed only to the "tails" of the (not perfect) Gaussian beam. These tails of lower current provide a greater degree of chemical enhancement (Fig. 3c), which becomes further enhanced by the more extensive tails of smaller spot sizes (Fig. 3d).

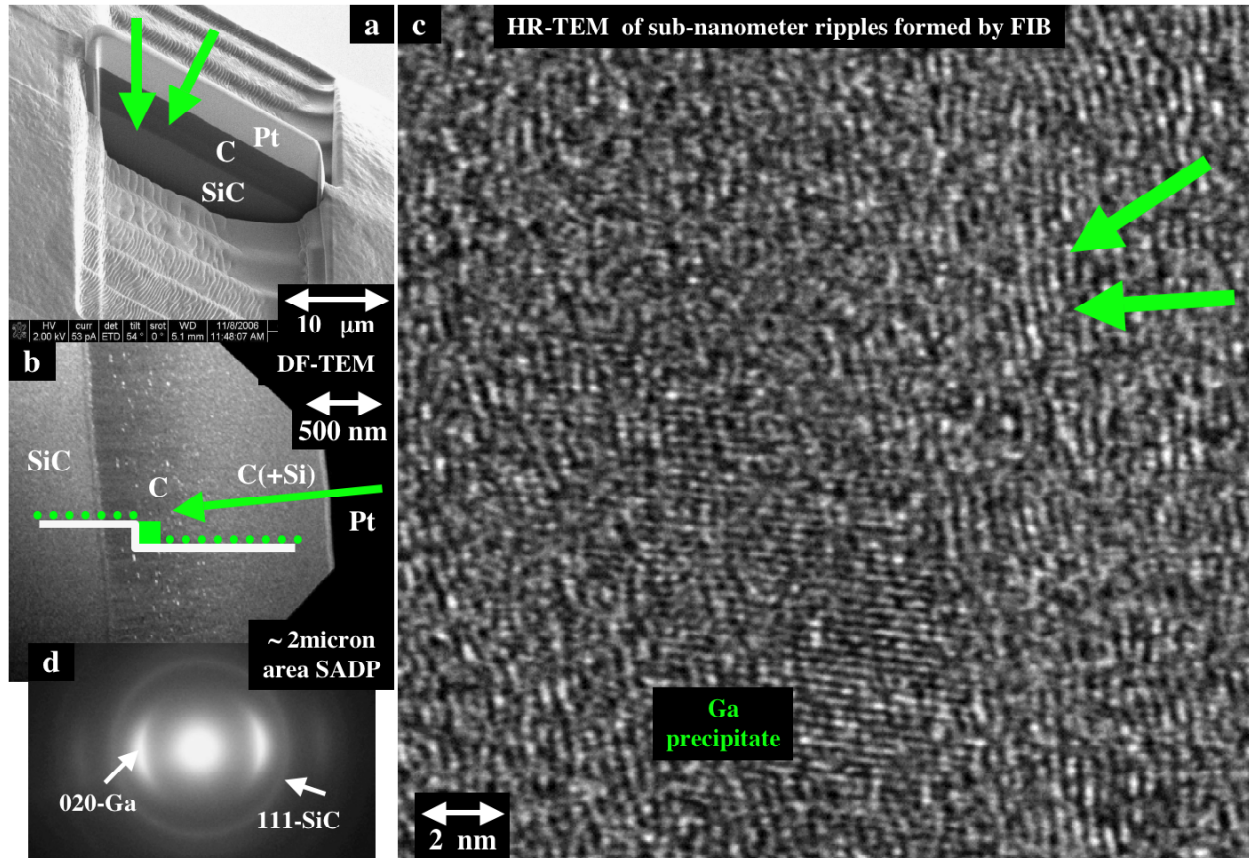


Figure 4: (a)-SEM image after FIB preparation of TEM section through protective Pt cap, double CVD-carbon coating, & SiC-fiber substrate. (Separate samples have FIB-30keV-Ga⁺ normal & inclined 30° to the coating-fiber interface. FIB polishing of TEM surfaces have ion beam incidence of 90.0°!) (b) Dark Field TEM with "g" parallel to substrate images Ga that precipitates on steps. (Not shown, "g" perpendicular to substrate highlights ripples.) (c) High Resolution TEM with lattice fringes from Ga precipitate and subnanometer ripples parallel to interface. (d) SAD of 2-micron area of polycrystalline SiC & 020-Ga ripples that form on the carbon surface of TEM lamella.

With a different goal than faster micromachining, the FIB now prepares TEM samples of CVD-carbon coatings on SiC fibers. FIB is often used to produce site-specific cross-section TEM samples. Figure 4a is an oblique SEM image after FIB sectioning through the protective overcoat Pt, the CVD-C coating, and

into the SiC (SCS-6) substrate. For TEM preparation, the two FIBed surfaces represent ion beam erosion approaching 90.0° incidence. Figures 4b through 4d are TEM data acquired respectively with Dark Field (DF) imaging, High Resolution (HR) imaging and Selected Area Diffraction (SAD). The TEM data is acquired normal to the thin lamella, meaning the FIB ions have impinged along the sample surface at an angle 90° to the TEM imaging beam. A bane of FIB preparation of TEM samples is an artifact parallel to the FIB and directional features in the TEM image appear as "curtaining". Since the samples may have directional features parallel to these curtaining artifacts, it is desirable to prepare samples with the FIB not normal to the substrate. Arrows in the figures indicate two different samples prepared with ion beams of different inclinations. However, the features observed in all three TEM data types exhibit an orientation relative to the substrate and not related to the orientation of the FIB. High angle ion sputtering (>80°) creates "steps" [11, 13], and even at 90° some small steps form. These steps trap impinging Ga, which crystallizes (Fig. 4b and 4c). The Ga ion etching also leads to small ripples on the surface, as viewed by HR-TEM. Typically wavy features can be common in a HR-TEM image due to astigmatism. The Ga precipitates are fortuitous as they provide a location to make sure the stigmatism is not present. Thus the ripples become visible everywhere between precipitates. The electron diffraction is more insightful of the long-range order of ripples, as it is acquired from a >2 micron area and exhibits an arc at a d-spacing of 0.38nm. (Diffraction rings of the polycrystalline SiC substrate provide an internal calibration in Fig. 4d to measure the ripple spacing, however, ripples only exist on the CVD-carbon region.)

The polycrystalline beryllium surface is FIBed normal to the surface; however polishing irregularities mean the FIB ranges $\pm 3^\circ$ in different locations of the surface. Because the low density of Be enhances ion channeling, the surface modulations that form are dependent on grain orientation. A well-ordered 2-dimensional array of dots form on one grain, but a less-ordered set of ripples form on the next grain (Fig. 5a). A third grain exhibits "pits" appearing almost the geometric inverse of the dots. Wavelengths also change near a grain boundary. However, the different etch rate of each grain orientation means that a height difference now exists at the grain boundary, and ripple wavelength near walls may increase due to redeposition [13]. FFT processing (Fig. 5c) of SEM images acquired normal to the surface, quantifies long-range order over many microns. Dots are often reported to self-assemble in close-packed (6-fold) arrangements; however, the periodic arrangement of Fig. 5c is closer to a HCP-[-1011] arrangement. An orientation relation (-2110) with the grain boundary appears to exist; however, none of the three main interfering ripples is parallel to the boundary as observed elsewhere [5]. Ga contamination is present on the eroded beryllium surface, and especially on the ripples of the TEM sample of Fig. 4; thus the high aspect ratio seen by SEM tilting (Fig. 5b) of these dots, pits, and ripples may have limited chemical compatibility for many uses. (A similar question of use arises for all FIB-produced ripples at the bottom of a FIB pit.) However, such surfaces may be imprinted onto other surfaces, thereby alleviating the Ga chemistry as well as transferring ripples to the tops of nanometer-scale site-specific pedestals.

DISCUSSION

Ripples and sputter yields are interdependent. Yield increases as ripples form; however, when ripples become large the yield can decay [9]. It is difficult for a FIB to drill a hole with aspect ratio >5 (depth-to-diameter), and even for aspect <0.1 a drop in yield is measured. As a hole deepens, the redeposition occurring within the hole increases, and ripples grow as the hole deepens. Thus redeposition becomes a source for ripple growth, akin to surface diffusion terms that modify ripples [2, 4, 6]. Redeposition is a significant term when a FIBed micron-scale hole reaches an aspect of ~ 0.1 , and redeposition may worsen for a nanometer-scale hole. Individual ripples may be viewed as nanometer-scale holes, and redeposition may occur within the ripples themselves. Computer modeling of atoms returning to the surface [14] may include electrical charge dependence and aspect ratio. A DualBeam typically uses the 2nd beam only for metrology, but controlled misalignments enable one beam to cut from a nearby small (zeptoliter-scale) source while the 2nd beam pastes onto a nearby substrate [6]. The 2nd beam typically patterns as a direct-write CVD process (either ion or electron beam assisted deposition); however it is also possible for the 2nd beam to induce ripples onto the new material as it deposits. Understanding how redeposition modifies

yield and ripple wavelength helps FIB control periodicity of surface modulations to $>400\text{nm}$ and $<0.4\text{nm}$.

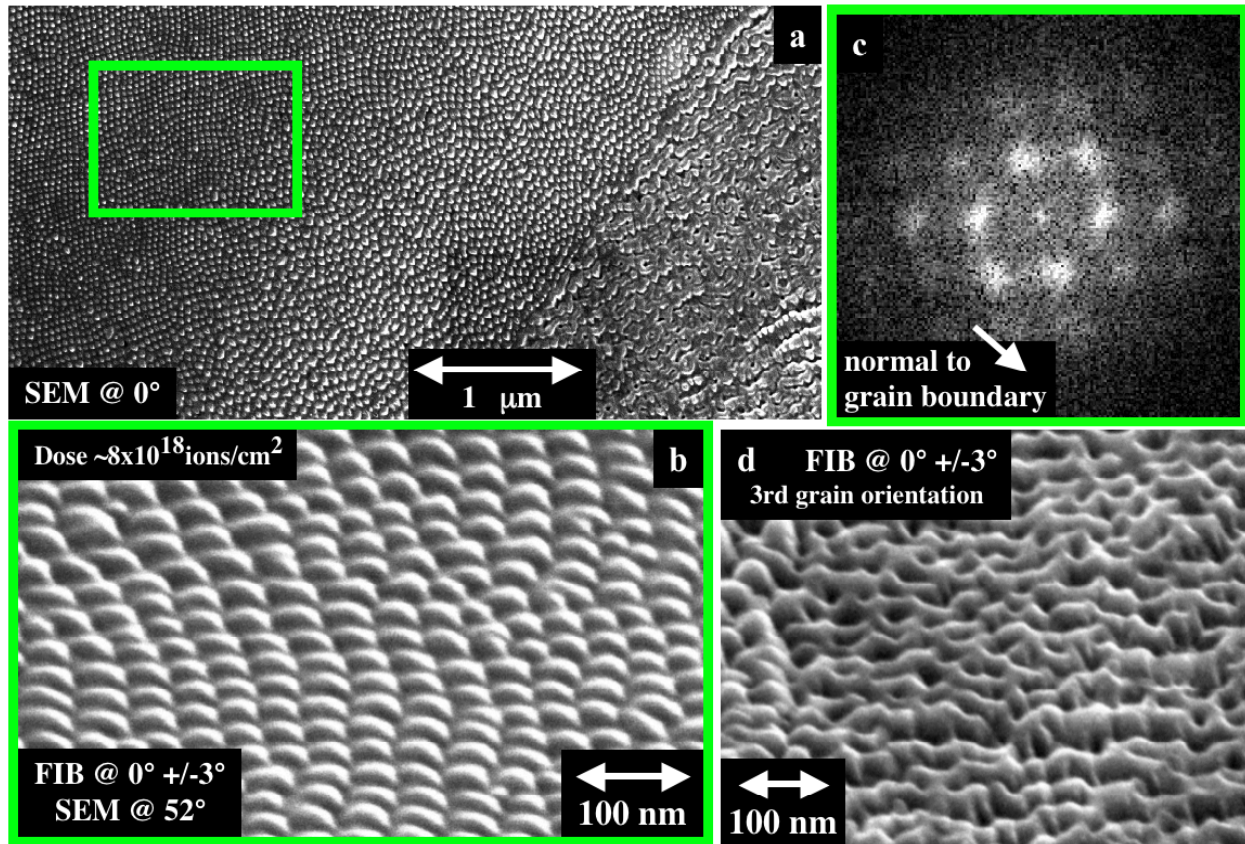


Figure 5: (a) SEM image of polycrystalline beryllium surface after FIB-30keV-Ga etching normal. (b) Higher magnification SEM oblique view depicts $<40\text{nm}$ dots of high aspect ratio. (c) FFT exhibits order over many microns and dependence on crystal orientation and nearby grain boundary. Different grain orientations provide varied patterns, some nearly the inverse of the mounds (d). Wavelength increases near grain boundary.

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